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Annealing conditions of $Bi_2Sr_2CaCu_2O_{8+x}$/CeO_2/r-plane sapphire by MOD method

S. Suzuki[a*], H. Shimakage[a], A. Kawakami[b], A. Saito[c], M. Takeda[d]

[a] *Graduate School of Science and Engineering, Ibaraki University, Hitachi, Ibaraki 316-8511, Japan*
[b] *National Institute of Information and Communications Technology, Kobe Research Laboratories, Kobe, Hyogo 651-2492, Japan*
[c] *Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan*
[d] *Graduate School of Science and Technology, Shizuoka University, Hamamatsu, Shizuoka 432-8011 Japan*

Abstract

We have been studying $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) thin films on CeO_2 buffered r-plane sapphire substrates by a metal organic decomposition (MOD) method. The deposited Bi-2212 thin films showed the c-axis oriented, and the in-plane orientation of the films showed 4-fold symmetry. However, we had a problem that Bi-2212 thin films were dissipation by thermal decomposition when the thin films were annealed above 840 °C in air atmosphere. In this study, we investigate the annealing conditions of Bi-2212 thin films. We found T_C of Bi-2212 thin films were dependence on the annealing condition such as a gas atmosphere and annealing times. The T_C of Bi-2212 thin film annealed at 840 °C for 60 min in nitrogen atmosphere was 68.5 K. On the other hand, in oxygen atmosphere, T_C was 65 K at the same annealing condition.

Keywords: Metal-organic decomposition; Bi-2212; Thin films; Sapphire substrate

1. Introduction

High-temperature superconductor (HTS) materials have been drawn attention for superconducting electronics applications after its discovery. HTS $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212), which was discovered in 1988, has higher critical temperature (T_C) than liquid nitrogen temperature (77 K) [1], and is being studied for some applications in many laboratories. To apply HTS materials to superconducting electronics, the fabrication of the Josephson junctions is waited. A Bi-2212 crystal structure stacks as layer-by-layer along the c-axis, and it behaves like as Josephson junctions. The junctions, which are called intrinsic Josephson junctions (IJJs), were discovered in 1992 by Kleiner *et al.* [2] and Oya *et al.* [3]. Recently, the IJJs are being studied in the application of THz wave oscillators with a high-power and high-frequency emission, and the experiments are done by using Bi-2212 single crystals. On the other hands, if a thin film technology is used for the fabrication of Bi-2212, it would be possible to integrate the Bi-2212 to some kinds of superconducting circuits. Bi-2212 thin film fabrication techniques have already been reported by a pulsed laser deposition (PLD) [4], a sputtering [5], a liquid phase epitaxy (LPE) [6], metal organic chemical vapor deposition (MOCVD) [7], and so on.

We have been studying a fabrications of the Bi-2212 thin films by a metal-organic decomposition (MOD) method, which has advantages of low running cost and the ability to fabricate large-sized films [8] [9]. For the high frequency applications, the substrate materials require a low dielectric constant and a low dielectric loss. Up to now, we have being studied Bi-2212 thin films on sapphire substrates, which are a candidate as a suitable substrate material because of its excellent high-frequency properties. However, it is difficult to deposit the Bi-2212 thin films directly on sapphire

*Corresponding author. Tel.:+81-294-38-5101; fax: +81-294-38-5275.
E-mail address: simakage@mx.ibaraki.ac.jp

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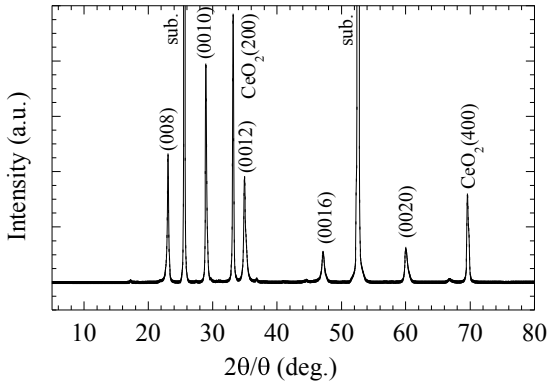

Fig. 1. The 2θ/θ XRD pattern of Bi-2212/CeO_2/r-plane sapphire fabricated in the nitrogen atmosphere.

substrates because of the large lattice mismatch and high reactivity between the Bi-2212 and the sapphire at high temperature. Therefore, we introduced CeO_2 thin films as a buffer layer to improve a lattice matching and prevent reactivity between the Bi-2212 and the sapphire. In our previous experiment [10], we have already confirmed the (00*l*) reflections of Bi-2212 on r-plane sapphire substrates buffered by CeO_2 thin films using by X-ray diffraction measurements. In the paper, we reported the annealing temperature dependence of the (00*l*) peak intensities by changing the annealing temperature, and a maximum value was obtained at 840 °C in air atmosphere. Moreover, we showed that the Bi-2212 thin films were grown epitaxially on the CeO_2 buffer layer by in-plane orientation measurements. The maximum T_C was obtained of 62.5 K. On the other hand, at >840 °C as annealing temperature in air atmosphere, we found that the surface of the Bi-2212 thin films tended to disappear after annealing.

In this report, we report on the investigation of the annealing conditions of Bi-2212 thin films on the r-plane sapphire with the CeO_2 buffer layer in various atmospheric conditions. Then, the prepared Bi-2212 thin films are evaluated by 2θ/θ patterns using X-ray diffraction (XRD), resistivity-temperature (ρ-T) measurements and the surface morphology observations by a scanning electron microscope (SEM).

2. Experimental

The Bi-2212 thin films were grown by a metal-organic solution (SKBSCCO-008, Kojundo Chemical Lab. SYMETRIX). The metal-organic solution was spin-coated on the substrate with 3000 rpm for 60 sec. The samples were prebaked on a hot plate at 120 °C for 2 min. The two-step annealing procedures were done separately. As a first step, the Bi-2212 films were annealed at 500 °C for 15 min; the temperature was fixed in the experiments. This annealed process is for decomposition of organic components by rapid thermal process. As a second step, the Bi-2212 films were annealed at 840 °C, and we compared with the thin film qualities for the second annealing time (T_f) of 30 and 60 min in an electric furnace. Furthermore, we investigated the Bi-2212 film qualities by changing the annealed atmospheric gases, such as nitrogen gas and oxygen gas. The thicknesses of the Bi-2212 thin films in this experiment were fixed of approximately 120 nm. The CeO_2 buffer layers were deposited by a sputtering system. Sputtering atmosphere and growth temperature were 10 Pa and 755 °C, respectively. A gas mixture ratio of Ar : O_2 was fixed of 32 : 11. After the deposition, the CeO_2 buffer layer was annealed ex situ at 1050 °C in air atmosphere for 2 hours in the electrical furnace. The thickness of the CeO_2 buffer layer was fixed of approximately 50 nm.

3. Results and discussion

3.1. Annealing in nitrogen atmosphere

We investigated the qualities of Bi-2212/CeO_2/r-plane sapphire substrates. The thin films were fabricated in the nitrogen atmosphere, and the annealing times were T_f=30 and 60 min. Fig. 1 shows the 2θ/θ XRD pattern of Bi-2212 thin film which was annealed for T_f=30 min. The (00*l*) reflections of Bi-2212 were observed. Next, we investigated the annealing time dependence of the (00*l*) peak intensities by changing the annealing time. However, there was little change in the (00*l*) peak intensity. Fig. 2 shows SEM images of Bi-2212/CeO_2/r-plane sapphire of (a) T_f=30 min and (b) T_f=60 min fabricated in nitrogen atmosphere. Many needle-like precipitates were appeared as shown in Fig. 2 (a). On the other hand, Fig. 2 (b) showed that the granulated fine precipitates were observed. The surface of Bi-2212 thin film annealed at 840 °C for 60 min in nitrogen atmosphere is smoother than that of annealed for 30 min, which infer

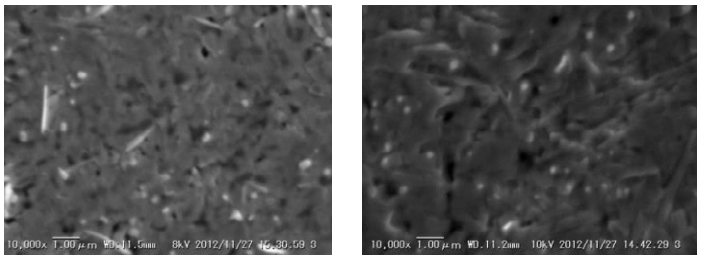

Fig. 2. Typical SEM images of Bi-2212/CeO_2/r-plane sapphire fabricated in N_2 atmosphere. (a) T_f=30 min, (b) T_f=60 min.

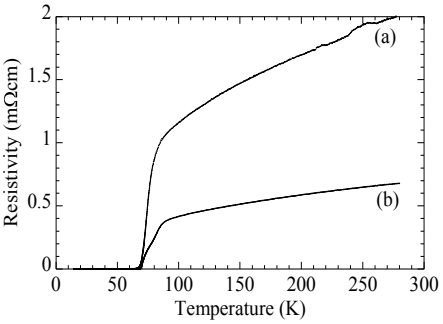

Fig. 3. The ρ-T of Bi-2212/CeO_2/r-plane sapphire. (a) T_f=30 min, (b) T_f=60 min.

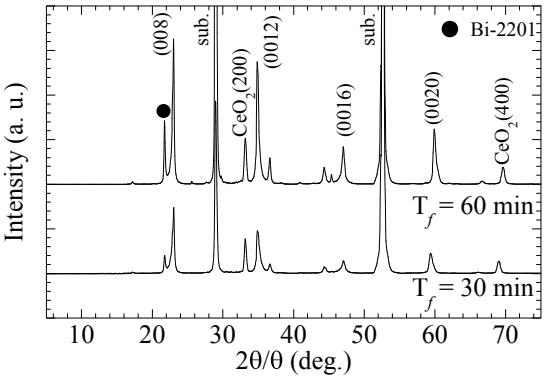

Fig. 4. The 2θ/θ XRD pattern of Bi-2212 thin film which was annealed for T_f=30 and 60 min.

that the long annealing time has the advantage of being kept large grains in thin films. To investigate more accurately, the detail investigation is going on. Moreover, we are planning to carry out a detailed analysis using an energy-dispersive X-ray spectroscopy (SEM-EDX) and in-plane alignment using a ϕ-scan.

Fig. 3 shows the temperature dependence of the resistivity of Bi-2212/CeO_2/r-plane sapphire. The T_C of Bi-2212 thin film annealed at 840 °C in nitrogen atmosphere was 65 K for T_f=30 min, and 68.5 K for T_f=60 min. The ΔT_C values were 13 and 18.5 K, respectively. We found that these values are large compared with the Bi-2212 single crystal. However, the resistivity of at the onset T_C along a-b plane of the films fabricated at T_f=60 min was 4.0×10^{-4} Ωcm. This value was comparable to that of the single crystal. We consider that the T_C of Bi-2212 thin films fabricated by MOD method could be increased by applying the optimal oxygen annealing.

3.2. Annealing in oxygen atmosphere

Next, we investigated the thin film quality after implementing the oxygen annealing. The thin films were fabricated in the oxygen atmosphere, and the annealing times were T_f=30 and 60 min. Fig. 4 shows the 2θ/θ XRD pattern of Bi-2212 thin film which was annealed for T_f=30 and 60 min. The (00*l*) reflections of Bi-2212 were observed. However, the results of 2θ/θ XRD patterns showed a mixture of 2201 phase. We consider that a mixture of Bi-2201 phase is due to thermal decomposition. Next, we investigated the annealing time dependence of the (00*l*) peak intensities by changing the annealing time. The (00*l*) peaks of Bi-2212 increased as T_f was increased up to 60 min. Fig. 5 shows SEM images of Bi-2212/CeO_2/r-plane sapphire of (a) T_f=30 min and (b) T_f=60 min fabricated in oxygen atmosphere. In Fig. 5 (a) and (b), the grains such as the precise islands were obtained. Annealing in oxygen atmosphere has already been reported [8]. There is an effect such as organic matter degradation. We consider that an effect of decomposing organic components makes smooth of surface of Bi-2212 thin film annealed in oxygen atmosphere. However, grain size of Bi-2212 does not change. Fig. 6 shows the temperature dependence of the resistivity of Bi-2212/CeO_2/r-plane sapphire. The T_C of Bi-2212 thin film annealed at 840 °C in oxygen atmosphere was 62.5 K for T_f=30 min and 65 K for T_f=60 min. The ΔT_C values were 18 and 16 K, respectively. We found that these values are large compared with the Bi-2212 single crystal. However, the resistivity of at the onset T_C along a-b plane of the films fabricated at T_f= 30 and 60 min were 5.0×10^{-4} and 3.8×10^{-4} Ωcm. This value was comparable to that of the single crystal. We consider that

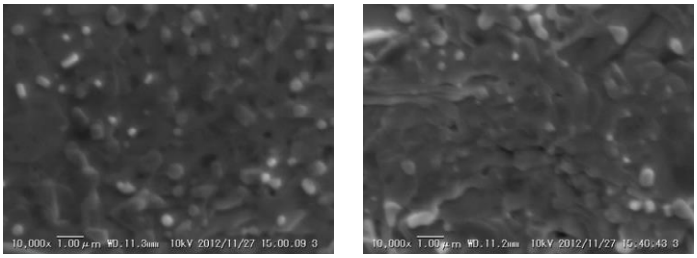

Fig. 5. Typical SEM images of Bi-2212/CeO_2/r-plane sapphire fabricated in O_2 atmosphere. (a) T_f=30 min, (b) T_f=60 min.

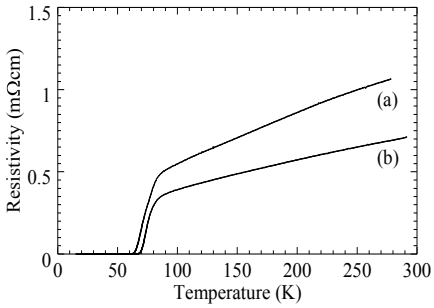

Fig. 6. The ρ-T of Bi-2212/CeO_2/r-plane sapphire. (a) T_f=30 min, (b) T_f=60 min.

the T_C of Bi-2212 thin films fabricated by MOD method could be increased by applying the oxygen annealing at optimal oxygen pressure. For the oxygen annealing, the longer annealing time seems to be better, such as nitrogen annealing. However, T_C is lower compared with the thin films with nitrogen annealing.

4. Conclusion

We investigate the annealing conditions of Bi-2212 thin films on the r-plane sapphire with the CeO_2 buffer layer by MOD method. In nitrogen atmosphere, the long annealing time grown the large size grains of Bi-2212 and the T_C was increased up 68.5 K. On the other hand, in oxygen atmosphere, the surface of Bi-2212 thin film was smoother than that annealed in nitrogen atmosphere. However, the grain size does not change when annealing long times. The detail experiments are undergoing for the investigation of annealing condition dependence.

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